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Hydroxymethylated resorcinol (HMR) priming agent for improved bondability of silicone modified wood glued with a polyvinyl acetate adhesive

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Subject A hydroxymethylated resorcinol (HMR) was used as a coupling agent to improve glueability of silicone (aminofunctional polydimethylsiloxane) modified pine sapwood (*Pinus sylvestris*) with polyvinyl acetate (PVAc). Priming with HMR did not significantly increase tensile shear strength of unmodified and silicone treated wood under dry conditions. Under wet conditions, tensile shear strength of the control specimens was increased by 37% and of the silicone modified specimens by 13%. Despite of higher shear strength under wet conditions, the primed silicone treated specimens displayed lower degree of wood failure than the unprimed treated specimens.

1 Introduction

Over the last years, a wide variety of silicon compounds have been applied to modify wood and to render the hydrophilic properties of wood more hydrophobic (Mai and Militz 2004, Donath et al. 2004, Donath et al. 2006, Weigenand et al. 2007). In practice, linear polydimethylsiloxanes (silicones) in particular are used as sealants on various surfaces. The presence of these compounds on the wood surface can delay or prevent the adhesive wetting of the surface and proper curing. Thus, joints that are made of silicone modified lumber are considered to have poor bonding properties and reduced shear strength.

Coupling agents can be used to improve bonding properties of wood surfaces. They are molecules with dual functionality. In use, one part of the molecule promotes adhesion to one surface (e.g. a wood surface) while another part of the molecule adheres to the surface of another material (e.g. an adhesive polymer) (Vick et al. 1995, 1998). Hydroxymethylated resorcinol (HMR) consists of mono-, di- and trihydroxymethylated resorcinol (Vick et al. 1995). It has been used as an effective coupling agent for adhesive bonding of wood. Surface treatment with HMR was found to improve bondline resistance to moisture and enhance adhesion to wood for epoxy, phenol formaldehyde, phenol resorcinol formaldehyde, polymer/isocynate, melamine formaldehyde, urea formaldehyde, and melamine formaldehyde adhesive (Vick et al. 1998).

This study investigates the effect of HMR priming on the tensile shear strength of silicone modified wood joints that are glued with polyvinyl acetate (PVAc) adhesive.

2 Experimental

Assembly blocks were prepared from kiln dried Scots pine (*Pinus sylvestris*) sapwood that was free of defects. The average density of wood blocks was 515 kg m^{-3} at 12% moisture content. Pine sapwood blocks (600 (long) × 130 × 6 mm^3) were treated with HANSA ASE 8130 (CHT R. Beitlich GmbH, Germany), a micro-emulsion with an ingredient content of 57% (40% silicone). The emulsion contains an amino-polydimethylsiloxane (silicone) compound bearing primary amino-propyl groups and a nitrogen content

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of 0.25%. The number of dimethylsiloxane subunits in the silicone molecules amounts to 300–400. The treatment was conducted as described previously (Weigenand et al. 2007) and resulted in a weight gain in the range of 25–32 kg m^{-3}. The active ingredient concentration was 5%. After the treatment, the specimens were conditioned in a climate chamber at 20 °C and 65% r.h.

Prior to the application of HMR or PVAc glue, the surface of the blocks was planed using a thicknesser. A 5% aqueous HMR solution was prepared according to Vick et al. (1996) and applied on silicone-treated and untreated blocks; the application rate for HMR was 170 g m^{-2}. Polyvinyl acetate (Jowacoll D4 with 5% Hardener (195.35); Jowat AG, Germany) was spread on the wood blocks and the assemblies were placed in a hydraulic press to exert required pressure of 0.5 N mm^{-2} (120 min) over the entire bonding area. The bond strength of the glued specimens was tested in longitudinal tensile shear according to the requirements of EN 302-1 (European Standard 1992). All specimens were tested under dry and wet conditions. Ten replicates were used for each treatment.

Analyses of variance (ANOVA) were conducted to determine sources of variation in tensile shear strength as affected by modifications, priming with HMR and testing conditions using the Statistical Analysis System (SAS) program (SAS Institute 2001). Specimens were grouped into two main groups which were dry and wet testing conditions. Comparisons of mean shear strengths were made by the Bonferroni (Dunn) t-test. When the differences exceeded the $\alpha = 0.05$ level of probability, the differences between means were considered significant.

3 Results and discussion

Mean dry and wet shear strengths of specimens ranged between 7.7–8.3 N mm^{-2} and 4.4–6.0 N mm^{-2}, respectively (Table 1). Silicone treatment did not affect the bonding strength of the specimens under dry and wet conditions, although the tested linear polydimethylsilicones are considered to impede gluing. It can, however, be assumed that planing specimens'surface using a thicknesser prior to gluing partly removed the silicone layer on the surface so that HMR or PVAc could directly get in contact with the wood substrate. Still, it was shown that the silicone microemulsion is able to penetrate deeply into the wood substrate and is deposited both in the lumens and in the cell wall (Weigenand et al. 2007). Under dry testing conditions, strength of the untreated controls and of the modified specimens was not significantly increased through priming with HMR within a confidence interval of $\alpha = 0.05$.

In contrast, priming increased wet strength of the control specimens by 37% and of the modified specimens by 13%, respectively (Table 1). Bonferroni t-test results revealed that these increases in wet strength were significant ($\alpha = 0.05$). The proportion of wood failure was low under wet conditions, except for primed untreated wood (60%, Table 1). Under wet conditions, the unprimed treated and untreated specimens displayed a higher proportion of wood failure than primed, silicone-treated wood, although the shear strength of the latter was significantly higher. Higher shear strength can be explained with reduction in water uptake due to silicon treatment. Hydrophobic silicone might have prevented the penetration of water molecules into the interface between PVAc and the wood surface.

Table 1 Mean values of tensile shear strength (N mm^{-2}), their Bon groupings and average wood failure (%)
Tabelle 1 Mittlere Zugscherfestigkeiten (N/mm^2), statistischer Test auf signifikante Unterschiede sowie durchschnittlicher Holzbruchanteil (%)

Sample ID	Dry Condition			Wet Condition		
	Mean	B.G.[a]	W.F.	Mean	B.G.[a]	W.F.
Control-Unprimed	7.73 ± 0.40	A	100	4.41 ± 0.19	A	30
Modified-Unprimed	8.08 ± 0.50	A	95	4.87 ± 0.20	B	20
Control-Primed	8.32 ± 0.67	A	80	6.03 ± 0.32	C	60
Modified-Primed	8.19 ± 0.52	A	75	5.52 ± 0.26	D	10

B.G.: Bon grouping ([a] Means with same letters are not statistically different), WF: Wood failure

4 Conclusion

The introduction of HMR priming on silicone modified wood surfaces did not increase the dry strength, but HMR priming was effective in improving the wet strength. From these results it can be concluded that the PVAc adhesive can be used to bond silicone modified wood only for interior uses. Overall, the results suggest that the use of the HMR priming agent for improving bonding properties of silicone modified wood needs further research. The bonding properties of other types of silicon compounds, e.g. amino silicone (macro emulsions), quaternary ammonium silicones, silane/siloxane, silicone-wax and silicate should be tested with different thermoplastic and thermosetting adhesives using not only HMR but also other surface agents.

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